

## Gold Nanoparticles Doping Graphene Sheets Nanocomposites Sensitized Screen-printed Carbon Electrode as a Disposable Platform for Voltammetric Determination of Guaiacol in Bamboo Juice

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An electrochemical sensor based on gold nanoparticles (Au) doping graphene sheets (GS) nanocomposites sensitized screen-printed carbon electrode (SPCE) as a disposable platform was developed for voltammetric determination of guaiacol (IUPAC name, 2-methoxyphenol) in bamboo juice. The SPCE was first modified by a dispersed solution of GS-Nafion (Nf), which was followed by electroless plating of Au on the surface to fabricate SPCE | GS-Nf/Au electrode. X-ray powder diffractometer (XRD), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were employed to characterize the synthesized GS and the construction processes of the modified electrode. The determination of guaiacol at the modified electrode was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in the phosphate buffer solution (PBS). Under the optimum experimental conditions, the peak currents obtained at +0.22 V from DPV were linearly dependent on the guaiacol concentrations in the range of  $1.0 \times 10^{-7}$  mol/L to  $1.5 \times 10^{-5}$  mol/L. The detection limit ( $3\sigma$ ) was  $5.4 \times 10^{-8}$  mol/L. The proposed modified electrode is sensitive, rapid, simple and disposable. In addition, the proposed sensor showed satisfactory recovery results toward the commercial bamboo juice samples.

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**Keywords:** Gold nanoparticles; Graphene sheets; Guaiacol; Screen-printed carbon electrode

## 1. INTRODUCTION

Bamboo juice is a kind of traditional Chinese herbs, which has been used as medicine with long history in China. As is well known, guaiacol with IUPAC name of 2-methoxyphenol is one of the most important effective components in bamboo juice [1]. Therefore, exploring the sensitive, rapid and simple analytical methods for precise monitoring of guaiacol is very important to the quality control and optimizing the preparation technology of bamboo juice samples.

Currently, the usual analytical methods mainly involve in gas chromatography (GC) [2], high performance liquid chromatography (HPLC) [3], LC-tandem mass spectrometry (LC-MS) [4] and GC-MS [5, 6]. However, those methods are somewhat cumbersome and not suitable for the in situ measurement due to the ponderous and complicated instruments. On the contrary, electrochemical sensor techniques have attracted growing interests in pharmaceutical analysis due to high-sensitivity, portability and low cost [7-9]. In more recent years, owing to their unique capabilities, such as high surface area, increased electron transport, low detection limit and better signal-to-noise ratio, many nano-materials including graphene sheets (GS) [10, 11] and gold nanoparticles (Au) [12, 13] have been used widely in nanotechnology-based pharmaceutical electrochemical sensors. Screen-printed carbon electrode (SPCE) is frequently used for the construction of simple portable devices for fast screening purposes and in-field/on-site monitoring, because of their low cost and easy integration into mass-production processes [14, 15]. Those studies demonstrated that GS and Au nanocomposites combined with SPCE could well meet the requirements of field detections of guaiacol.

As far as we know, Au doping GS nanocomposites sensitized SPCE has never been used for the voltammetric determination of guaiacol. In this paper, we report on an ultrasensitive guaiacol electrochemical sensor based on GS-Nafion (Nf)/Au nanocomposites modified SPCE (SPCE | GS-Nf/Au). The resulting modified electrode combines the advantages of GS, Au and SPCE. In addition, the fabrication of the modified electrode is sensitive, rapid, simple and disposable. Finally, the modified electrode has been successfully applied to analyze guaiacol in bamboo juice samples with good recovery and accuracy, demonstrating its potential use for real sample analysis.

## 2. EXPERIMENTAL

### 2.1. Reagents

Graphite powder was obtained from Green Battery Material Limited Company (Changsha, China). Guaiacol was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd (No: 020050318). San qing-shen bamboo juice oral liquid was purchased from Hunan Zhengqing Pharmaceutical Group Co., Ltd (No: 1104305). Nf solution, HAuCl<sub>4</sub>, 30% H<sub>2</sub>O<sub>2</sub> solution and other chemicals were of analytical-reagent grade and used without further purification were obtained from Sinopharm Medicine Holding Co., Ltd (Shanghai, China). The 0.1 mol/L phosphate buffer solution (PBS) at various pH values were prepared by mixing the stock solutions of 0.1 mol/L NaH<sub>2</sub>PO<sub>4</sub> and 0.1 mol/L Na<sub>2</sub>HPO<sub>4</sub> with different proportion. Doubly distilled water (18.2 MΩ resistance) was used throughout.

## 2.2. Apparatus

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (CHI Instruments, Shanghai, China). SPCE was purchased from DropSens corporation (Spain, the working electrode was modified, the auxiliary and reference electrode was printed carbon and Ag/AgCl electrode, respectively.). The morphology of different electrodes was characterized by the scanning electron microscopy (SEM, Hitachi S-4800). The X-ray powder diffractometer (XRD, Rigaku Ultima IV, Cu K $\alpha$  radiation) was used to determine the phase purity and crystallization degree.

## 2.3. Preparation of GS solution

Firstly, the graphite oxide was synthesized from natural graphite powder according to the literature with a modified Hummers method [16, 17]. Then, exfoliation of graphite oxide to graphene oxide (GO) was achieved by vigorously ultrasonication of the dispersion for 30 min. Finally, a bright yellow homogeneous aqueous dispersion was obtained. As a large number of carboxyl, hydroxyl hydrophilic groups have been introduced between the layers of carbon atoms, GO is soluble in water. The resulting homogeneous dispersion GO (0.1 g) was mixed with 50  $\mu$ L hydrazine solution. After being vigorously shaken or stirred for a few minutes, the solution was stirred for 24 h at the temperature of 80  $^{\circ}$ C to form GS. Because GS tend to form irreversible agglomerates or even restack to graphite through strong  $\pi$ - $\pi$  conjugation or Van der waals interaction, it is difficult for GS to be directly dispersed into solvent to form a uniform dispersion, which brings about the difficulty for the construction of electrochemical sensing platforms. Herein, Nf was selected as a stabilizer to disperse GS into an aqueous solution [18].

## 2.4. Preparation of the modified electrode

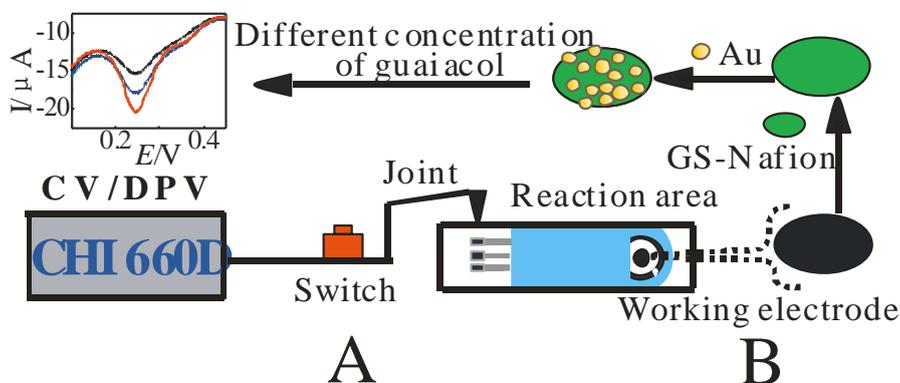
100.0 mg of GS was dispersed into 100.0 mL of 0.2% Nf solution to form a homogenous dispersion under vigorously ultrasonication for about 0.5 h. 8  $\mu$ L of the resulting GS-Nf dispersion was dropped onto the surface of the SPCE and was kept at room temperature till dry (labeled as SPCE | GS-Nf). The modification of Au onto SPCE | GS-Nf electrode was achieved by electroless plating according to the literature [19]. After modification, the electrode (labeled as SPCE | GS-Nf/Au) was thoroughly rinsed with water and kept at room temperature for further use.

## 2.5. Analytical procedures

1.0 mL of PBS (0.1 mol/L, pH 6.0) with appropriate amount of guaiacol standard solution (final concentration of guaiacol was ranged between  $1.0 \times 10^{-7}$  mol/L to  $1.5 \times 10^{-5}$  mol/L) were added into the reaction area of the modified electrode and was deposited at +0.3 V under stirring for 60 s. Following the preconcentration step, DPV was applied a negative-going potential scan over the range

of +0.1 to +0.5 V and recorded the stripping peak of guaiacol at +0.22 V. The schematic diagram of the electrochemical sensor apparatus and the surface of working electrode were showed in Fig. 1.

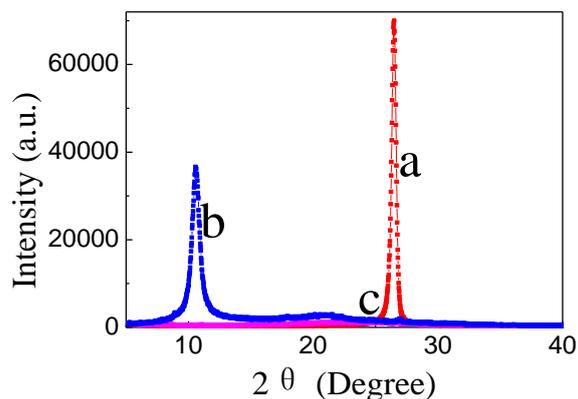
The real samples were filtered through a 0.22  $\mu\text{m}$  millipore membrane firstly, and the recommended procedure was followed as mentioned above. The results were compared with the standard addition method to confirm the reliability of this method.



**Figure 1.** Schematic diagram of the electrochemical sensor apparatus (A) and the surface of working electrode (B).

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of the synthesized GS



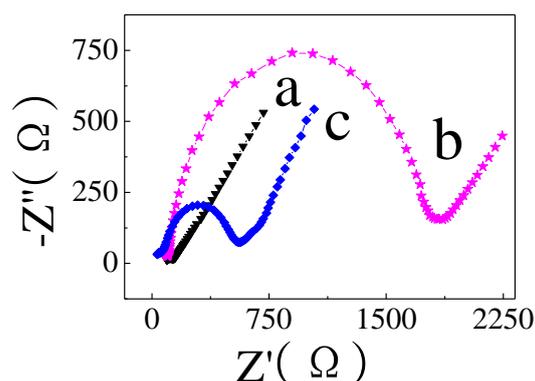
**Figure 2.** XRD patterns of graphite (a), GO (b) and GS (c).

The phase structures of the samples were examined by XRD measurements. It is clearly seen in Fig. 2a that the typical but strong diffraction peak (002) of graphite locates at  $26^\circ$ . In Fig. 2b, the typical diffraction peak (002) of graphite shifts to lower angle ( $2\theta=10.6^\circ$ ), which is ascribed to the introduction of various oxygenic functional groups (epoxy, hydroxyl, carboxyl and carbonyl) attached on both sides and edges of graphite sheets [20]. Fig. 2c shows the XRD of GS. The weak diffraction

peaks at about  $2\theta=23^\circ$  are in good agreement with graphite [21, 22]. This is due to the partial removal of the oxygen-containing functional groups during reduction process, which means the partially reduction of GO to GS and restacked into a disordered crystalline structure.

### 3.2. Electrochemical impedance study of different electrode

The capability of electron transfer of different electrodes was investigated by electrochemical impedance spectra (EIS), shown in Fig. 3. In which the Nyquist plots are shown with the real part ( $Z'$ ) on the X-axis and the imaginary part ( $-Z''$ ) on the Y-axis. The spectrum includes a semicircle part and a linear part, of which the semicircle part at high frequencies corresponds to the electron transfer limited process and the linear part at low frequencies corresponds to the diffusion process. The diameter of the semicircle portion corresponding to the electron transfer limited process equals to the electron transfer resistance ( $R_{ct}$ ). It can be seen that EIS of the SPCE is composed of a semicircle and a straight line featuring a diffusion limiting step of the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  processes (Fig. 3a). With the GS-Nf film modified onto SPCE, the diameter of the semicircle increased significantly (Fig. 3b). It shows the consistency with the fact that the insulation of the polymer Nf film interrupts the electron transfer with increased  $R_{ct}$ . Compared with the EIS of SPCE | GS-Nf electrode, the diameter of the semicircle of SPCE | GS-Nf/Au electrode (Fig. 3c) decreased remarkably. This demonstrates that the electrochemical activity of SPCE | GS-Nf/Au electrode is higher than that of SPCE | GS-Nf electrode. All above indicate that GS-Nf and Au can successfully immobilize on the surface of SPCE.

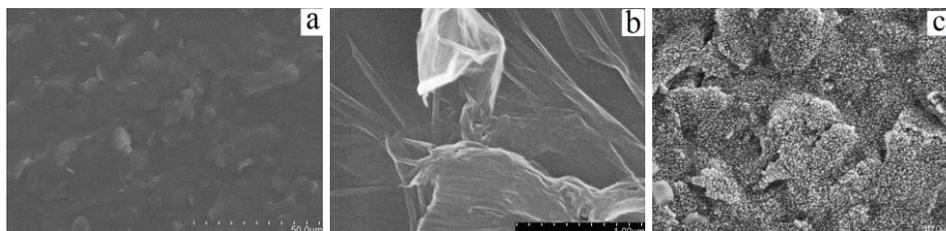


**Figure 3.** EIS of SPCE (a), SPCE | GS-Nf (b) and SPCE | GS-Nf/Au (c) electrode in 0.1 mol/L KCl solution containing 10 mmol/L  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (1:1).

### 3.3. Characterization of different electrodes' surface

Fig. 4a appears the flake graphite on the surface of SPCE. As indicated in the magnified SEM image, the surface of SPCE | GS-Nf electrode exhibits a few thin wrinkles (Fig. 4b), the observation for the edge of the nanosheets confirms the layered structure of GS [23]. With the electroless plating of Au onto SPCE | GS-Nf electrode, uniform Au of about 30 nm to 100 nm in average diameter formed

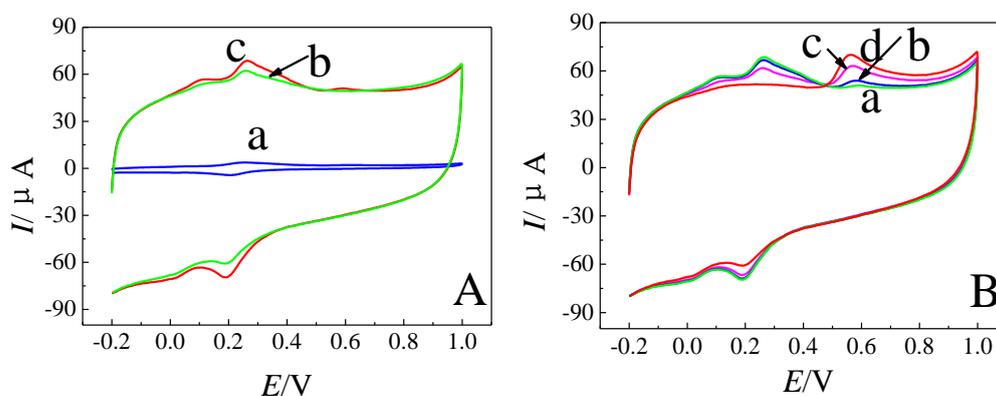
randomly on the sheets (Fig. 4c). Obviously, the generated Au was homogenously distributed onto the GS-Nf matrix, constructing a monodispersed GS-Au based ensemble for the stripping analysis of guaiacol.



**Figure 4.** SEM images of SPCE (a), SPCE | GS-Nf (b) and SPCE | GS-Nf/Au (c) electrode.

### 3.4. Electrochemical behavior of guaiacol on different electrode

Fig. 5A shows the CV curves of  $1.0 \times 10^{-5}$  mol/L guaiacol in PBS on different electrode. The response of SPCE (A-a) is poor with one cathodic peak ( $E_{pc}=+0.22$  V) and two anodic peaks ( $E_{pa1}=+0.25$  V,  $E_{pa2}=+0.58$  V). However, the signals of SPCE | GS-Nf (A-b) and SPCE | GS-Nf/Au (A-c) electrodes are both remarkably enhanced than that at the SPCE. That is because of both GS and Au have unique electrochemical properties and large surface area, which could accelerate the transfer rate of electron and provide more reaction sites [16]. Meanwhile, nano-sized GS and Au are both negatively charged, they could enrich the positively charged guaiacol on the surface of electrode through electrostatic attraction. As can be seen from curve A-c, the peak current of guaiacol at SPCEs | GS-Nf/Au electrode is more intense than A-a and A-b. It clearly confirms that the GS-Nf and Au are essential to amplify the stripping current and improve the sensitivity. Moreover, with CVs continuing (Fig. 6B, a-b-c-d), the anodic peak of guaiacol on the modified electrode at  $E_{pc}=+0.25$  V decreased. Meanwhile, the cathodic peak at +0.22 V and anodic peak at +0.58 V increased gradually until stability.



**Figure 5.** CVs of SPCE (a), SPCE | GS-Nf (b), SPCE | GS-Nf/Au (c) with  $1.0 \times 10^{-5}$  mol/L guaiacol in 0.1 mol/L PBS (A) and the first to fourth cycle (B).

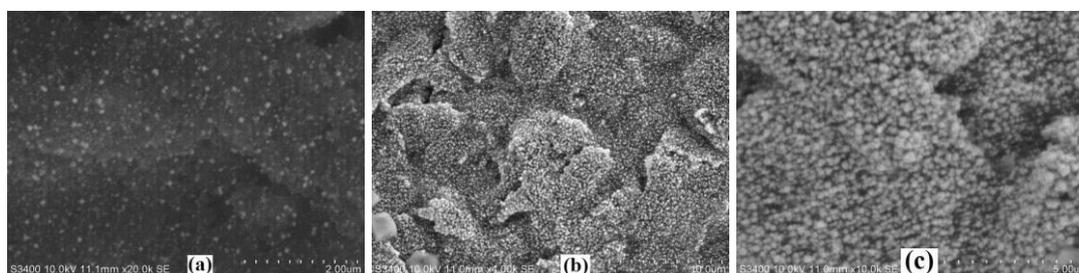
### 3.5. Optimization of the electrode modification

#### 3.5.1. The effect of the amount of GS-Nf solution

The amount of GS-Nf solution on the modified electrode was a critical parameter for electrochemical reaction of guaiacol. Experiments were carried out to choose the amount of GS-Nf solution used. A series of SPCE | GS-Nf electrodes were prepared with different volume of GS-Nf solution, and then these electrodes were modified with the same amount of Au by electroless plating to obtain a series of SPCE | GS-Nf/Au electrodes. The peak current of  $1.0 \times 10^{-5}$  mol/L guaiacol increased with the volume of GS-Nf solution modified onto the electrode at first up to 8  $\mu$ L and then decreased. Higher amount of GS-Nf solution caused broadening of voltammogram and decreased the intensity of peak current. So, 8  $\mu$ L of GS-Nf solution was used to prepare the modified electrode.

#### 3.5.2. The effect of the sizes of Au

Fig. 6 shows the SEM images of the as-formed Au on electrode. With electroless plating time increased up to 30 s, small Au and low coverage onto the electrode was observed (Fig. 6a). While the time was increased to 60 s, the Au would be continuously generated (Fig. 6b). The enhanced surface area from the modification of Au enables more available active sites on the electrode surface for guaiacol deposition. However, as the time increased to 90 s, the Au finally aggregated (Fig. 6c), resulting in the decreased sensing performance. Thus, electroless plating time of 60 s was optimal for the preparation of Au modified electrode. Gu [24] found that the small size of the Au (about 50~100 nm) can accelerate the electron transfer and allowing to facilitate the electrons transmission through the Au passage. It would be most extent amplification of the response current. Therefore, the synthesized of monodisperse electroless plating Au particle sizes of 30 nm to 100 nm by this method could greatly amplify response current.

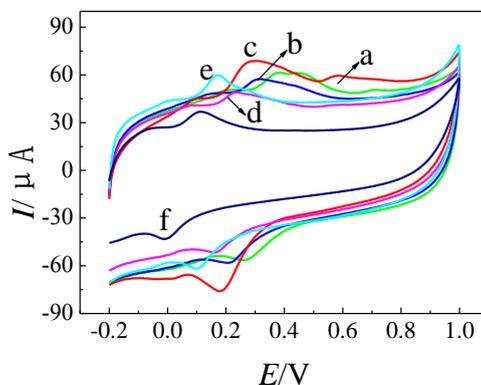


**Figure 6.** SEM images of SPCE | GS-Nf electrode with electroless plating time of 30 s (a), 60 s (b) and 90 s (c).

#### 3.5.3. The effect of supporting electrolyte and pH

Guaiacol has different electrochemical behaviors in different electrolytes. The effects of some electrolytes, such as 0.1 mol/L acetate buffer solution (NaAc-HAc),  $\text{NH}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_4\text{Cl}$  and PBS on

stripping peak currents of  $1.0 \times 10^{-5}$  mol/L guaiacol was studied. The results showed that guaiacol has the best electrochemical responses in PBS. When the measurements were performed in this electrolyte, the largest stripping peak current, the lowest background current and the best shape of peak were obtained. The influence of pH on the determination of guaiacol was also investigated (Fig. 7). At first, the peak current increased as the pH from pH 4.5 to 6.0. Continuous increased of pH led to a decrease of the peak current. Taking account of the factors above, 0.1 mol/L PBS (pH=6.0) was used for the supporting electrolyte, which in agreement with the previous report [25].



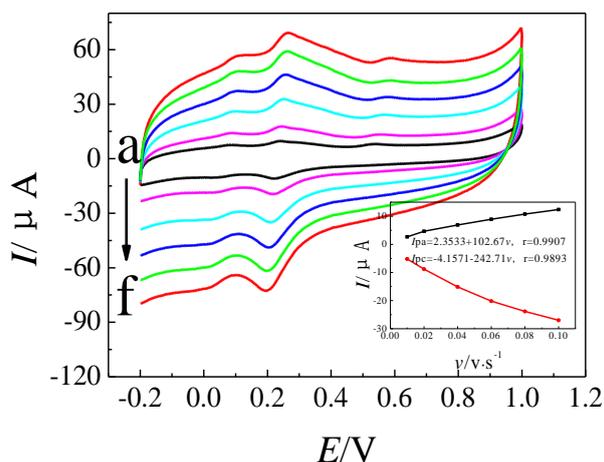
**Figure 7.** CVs of  $1.0 \times 10^{-5}$  mol/L guaiacol obtained in PBS with pH values of 4.5 (a), 5.5 (b), 6.0 (c), 6.5 (d), 7.5 (e) and 8.5 (f).

### 3.5.4 The effect of accumulation potential and time

The effect of the accumulation potential on the peak current of  $1.0 \times 10^{-5}$  mol/L guaiacol after 60 s accumulation was studied in the potential range from +0.1 V to +0.8 V and the obtained results shown that the accumulation potential shifts from +0.1 V to +0.3 V, the stripping peak currents increased. As the accumulation potential became more positive, the peak current reduced. To obtain the good sensitivity, +0.3 V was used as the optimal accumulation potential for the subsequent experiments. The sensitivity of the proposed electrode was undoubtedly improved by the accumulation time. With the increase of the accumulation time, the response of the stripping peak currents of guaiacol increased linearly with the preconcentration time due to the increased amount of analytes on the modified electrode. However, the stripping peak currents value changed slightly to 60 s because of the rapid surface saturation, which lowers the upper detection limit. Therefore, 60 s was chosen as the optimal accumulation time.

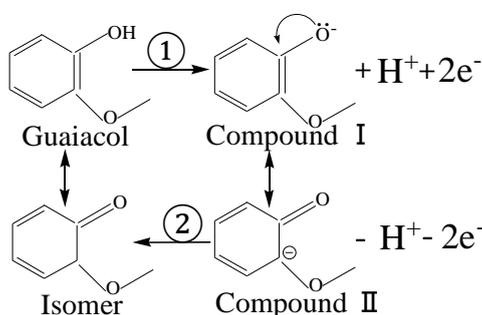
### 3.6. The redox mechanism of guaiacol on SPCE | GS-Nf/Au electrode

Fig. 8 displays the CVs of the modified electrode in 0.1 mol/L pH=6.0 PBS containing  $1.0 \times 10^{-5}$  mol/L guaiacol at various scan rate. Both the reduction and oxidation currents increased with the scan rate and displayed good linear relationship between currents and scan rates as shown in inset, inferring that the electrochemical reaction could be governed by a typical adsorption-controlled process [26].



**Figure 8.** CVs of  $1.0 \times 10^{-5}$  mol/L guaiacol acquired on SPCE | GS-Nf/Au electrode in 0.1 mol/L PBS at scan rate of 10 (a), 20 (b), 40 (c), 60 (d), 80 (e) and 100 (f) mV/s.

As can be seen in Fig. 8, with pH value of the solution increasing, the redox peak shifted negatively, which indicates that the redox reactions involve the protons [27]. The formal potential changed linearly, depending on a pH from 4.5 to 8.5, and the proton number was estimated about 1. According to the discussion mentioned above, the redox of guaiacol belongs to a two-electron and one-proton process. The possible redox mechanism of guaiacol on the modified electrode was shown in Scheme 1. During the first redox process (1), guaiacol reacted with the electrode at +0.25 V to form the first intermediate (Compound I). Compound I was unstable and could be converted into Compound II at +0.58 V during the second redox process (2). Compound II was subsequently reduced back to the isomer of guaiacol during the third redox process (2) by losing two electron and one proton at +0.22 V.

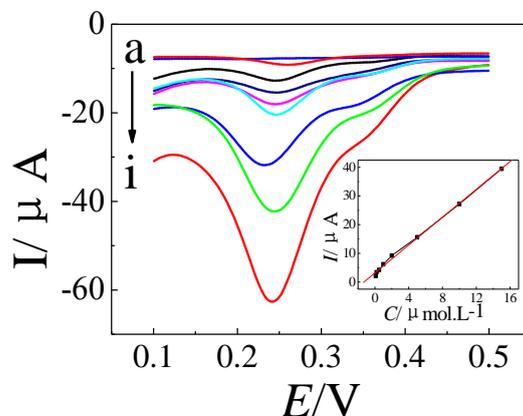


**Scheme 1.** The redox mechanism of guaiacol on SPCE | GS-Nf/Au electrode.

### 3.7. The detection of guaiacol on SPCE | GS-Nf/Au electrode

Under optimal experimental conditions, the SPCE | GS-Nf/Au electrode was applied for the successive determination of guaiacol by DPV. Fig. 9 showed the DPV responses of the SPCE | GS-

Nf/Au electrode toward guaiacol at different concentrations. Well-defined current peaks proportional to the concentration of guaiacol ( $C_{\text{guaiacol}}$ ) was observed in the ranges of  $1.0 \times 10^{-7}$  mol/L to  $1.5 \times 10^{-5}$  mol/L with the linearization equation:  $\Delta i_p (\mu\text{A}) = 3.1590 + 2.4298 C_{\text{guaiacol}} (\mu\text{mol/L})$  ( $r = 0.9970$ ). The detection limit of  $5.4 \times 10^{-8}$  mol/L was obtained with the calculation based on signal-noise ratio equal to 3 ( $3\sigma$ ).



**Figure 9.** DPVs of SPCE | GS-Nf/Au electrode for different guaiacol concentrations (a–i): 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 15.0  $\mu\text{mol/L}$ . Inset is the relationship of DPV current to  $C_{\text{guaiacol}}$ .

### 3.8. Repeatability, stability and selectivity of SPCE | GS-Nf/Au electrode

The repeatability of the modified electrode was valued at a guaiacol concentration of  $1.0 \times 10^{-5}$  mol/L with the same SPCE | GS-Nf/Au electrode. The relative standard deviation (*R.S.D.*) was 3.1% for five successive assays. The electrode-to-electrode repeatability was determined in the presence of same concentration guaiacol with five different SPCE | GS-Nf/Au electrodes, prepared independently. It showed an acceptable reproducibility with a *R.S.D.* of 3.4%.

The stability of SPCE | GS-Nf/Au electrode was also examined during storage in a drying state at 4 °C. It was found that the current response remained nearly 93% of the initial value over 4 weeks, indicating long-term stability.

The effect of substances that might interfere with the response of the modified electrode was also studied. The selectivity of the modified electrode was examined in presence of  $1.0 \times 10^{-5}$  mol/L guaiacol under relative error less than  $\pm 5\%$ . The addition of 100-fold concentration of NaCl, KCl, glucose, cysteine, lactate, lysine did not cause observable interference.

### 3.9. Application on real samples

In order to test the validity of this method, the proposed procedure was applied for determination of guaiacol in real bamboo juice oral liquid samples. Before experiments, the real samples were diluted several times with doubly distilled water and filtered through a millipore membrane filter with an average pore diameter of 0.22  $\mu\text{m}$ . Recovery tests method was used to

examine the reliability and accuracy of this method. The guaiacol content of different samples and recoveries of added analyte were evaluated and the results showed that it was possible to determine the guaiacol concentration in real samples by using the proposed method (Tab. 1).

**Table 1.** Determination results of guaiacol in real samples (mol/L)

Sample	This method	Added	Found	R.S.D (%) , n=6	Recovery (%)
1	$7.28 \times 10^{-7}$	$2.00 \times 10^{-6}$	$2.75 \times 10^{-6}$	3.60	101.0
2	$7.47 \times 10^{-7}$	$2.00 \times 10^{-6}$	$2.71 \times 10^{-6}$	3.52	98.1
3	$7.32 \times 10^{-7}$	$2.00 \times 10^{-6}$	$2.77 \times 10^{-6}$	2.71	102.0

#### 4. CONCLUSIONS

In summary, a novel disposable electrochemical sensor for determination of guaiacol based on Au doping GS nanocomposites sensitized SPCE was fabricated. The proposed modified electrode has high surface activity due to being modified with composite nano-particles, which could amplification the response current. It also showed the merits of disposable design, low cost, good reproducibility and long term stability. The proposed method was successfully applied for the determination of guaiacol in real samples. It may open up a new approach to explore GS-Au-based nanocomposites materials for pharmacies analysis. The technology platform has generality, which could be further used in the determination of other pharmacies and could be a beneficial supplement to GC, HPLC or GC-MS.

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#### References

1. B.L. Chen, M. Zhu and F.Q. Zhou, *Chin. Traditional Patent Med.* 25 (2003) 482.
2. B. Liu, Y.B. Zhu and Z.F. Yao, *Guiding J. Traditional Chin. Med. Pharm.*, 2 (2007) 75.
3. Y.X. Zhou and Y.B. Zhu, *Guiding J. Traditional Chin. Med. Pharm.*, 6 (2009) 77.
4. K.A. Dungey, Y. Hayasaka and K.L. Wilkinson, *Food Chem.*, 126 (2011) 801.
5. P.R. Pérez-Cacho, M.D. Danyluk and R. Rouseff, *Food Chem.*, 129 (2011) 45.
6. Ó. Ezquerro, Á. Garrido-López and M.T. Tena, *J. Chromatogr. A.*, 1102 (2006) 18.
7. X. Yang, N. Gan, D.H. Xie, W.G. Wen and N.X. Luo, *Acta Chim. Sinica.*, 68 (2010) 75.
8. R.N. Goyal, V.K. Gupta and S. Chatterjee, *Sens. and Actuators, B.*, 149 (2010) 252.
9. L. Tan, K.G. Zhou, Y.H. Zhang, H.X. Wang, X.D. Y.F. Guo and H.L. Zhang, *Electrochem. Commu.*, 12 (2010) 557.
10. P. Martin, *Chem. Soc. Rev.*, 39 (2010) 4146.

11. X. Yang, F. Wu, D.Z. Chen and H.W. Lin, *Sens. and Actuators, B.*, 192 (2014) 529.
12. J.W. Wang, L.P. Wang, J.W. Di and Y.F. Tu, *Talanta*, 77 (2009) 1454.
13. S.L. Yang, Y.L. Yin, G. Li, R. Yang, J.J. Li and L.B. Qu, *Sens. and Actuators. B.*, 178 (2013) 217.
14. O.D. Renedo, M.A. Alonso-Lomillo and M.J. Arcos Martinez, *Talanta*, 73 (2007) 202.
15. X. Yang, F.B. Xiao, H.W. Lin, F. Wu, D.Z. Chen and Z.Y. Wu, *Electrochim. Acta.*, 109 (2013) 750.
16. K.F. Zhou, Y.H. Zhu, X.L. Yang, J. Luo, C.Z. Li and S.R. Luan, *Electrochim. Acta.*, 55 (2010) 3055.
17. H. Bai, Y.X. Xu, L. Zhao and G.Q. Shi, *Chem. Commun.*, 45 (2009) 1667.
18. H.S. Yin, Y.L. Zhou, Q. Ma, S.Y. Ai, P. Ju, L.S. Zhu and L.N. Lu, *Process Biochem.*, 45 (2010) 1707.
19. Y. Kong, H.W. Chen, Y.R. Wang and S.A. Soper, *Electrophoresis*, 27 (2006) 2940.
20. H.L. Guo, X.F. Wang, Q.Y. Qian, F.B. Wang and X.H. Xia, *ACS Nano*, 3 (2009) 2653.
21. Y.G. Zhou, J.J. Chen, F.B. Wang, Z.H. Sheng and X.H. Xia, *Chemi. Commun.*, 46 (2010) 5951.
22. C. Nethravathi and M. Rajamathi, *Carbon*, 46 (2008) 1994.
23. H.F. Yang, F.H. Li, C.S. Shan, D.X. Han, Q.X. Zhang, L. Niu and A. Ivaska, *J. Mater. Chem.*, 19 (2009) 4632.
24. H.Y. Gu, A.M. Yu and H.Y. Chen, *J. Electroanal. Chem.*, 516 (2001) 1119.
25. Y. Wu, M. Huang, N.N. Song and W.B. Hu. *Anal. Methods*, 6 (2014) 2729.
26. Y. Huang, C.M. Cheng, X.Q. Tian, B.Z. Zheng, Y. Li, H.Y. Yuan, D. Xiao and M.M.F. Choi, *Electrochim. Acta.*, 89 (2013) 832.
27. X.H. Kang, J. Wang, H. Wu, J. Liu, I.A. Aksay and Y.H. Lin, *Talanta*, 81 (2010) 754.